

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 10/10/00	3. REPORT TYPE AND DATES COVERED Final Report 08/01/96 - 07/31/99		
4. TITLE AND SUBTITLE Metallo-Network Polymers: Biomimetic Metal Binding/Recognition Sites		5. FUNDING NUMBERS N00014-96-1-1216		
6. AUTHOR(S) A. S. Borovik				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry University of Kansas Lawrence, KS 66045		8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy St. Arlington, VA 22217-5000		10. SPONSORING / MONITORING AGENCY REPORT NUMBER		
11. SUPPLEMENTARY NOTES Distribution Unlimited				
12a. DISTRIBUTION / AVAILABILITY STATEMENT		12b. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words)  New composite materials have been designed and fabricated with funds provided by ONR/DESPCoR grant N00014-96-11216. Copolymers have been developed from molecular precursors, which dispersed metal complexes throughout highly crosslinked, porous organic hosts. These materials have been applied to problems in gas storage/release and transport, and sensor technology. They are durable, function in water and organic solvents, and maintain their binding site structures. Materials that reversibly bind O <sub>2</sub> and NO have been designed and synthesized. Rapid and reversibly dioxygen binding is observed with dioxygen binding capacities of ~160 µmol O <sub>2</sub> /g polymer. Biomedical applications include artery (smooth muscle) relaxation under biologically relevant conditions, which is induced by the release of NO from a NO-containing polymer. This NO-releasing material also inhibits platelet formation in an in vitro assay.				
14. SUBJECT TERMS			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT U1	

20001025 022

## FINAL PROGRESS REPORT

Grant #: N00014-96-11216

PRINCIPAL INVESTIGATOR: A. S. Borovik

INSTITUTION: University of Kansas

EMAIL: aborovik@ukans.edu

GRANT TITLE: Metallo-Network Polymers: Biomimetic Metal Binding/Recognition Sites

REPORTING PERIOD: 01 August 1996 - 31 July 1999

AWARD PERIOD: 01 August 1996 - 31 July 1999

OBJECTIVE: To design and synthesize new abiotic materials that mimic the functional properties found in metalloproteins and are active under non-biological conditions. Materials that rapidly and reversibly bind  $O_2$ , NO, and CO are desired, which can be applied to problems in gas storage/release and transport, chemical sensing, and catalysis.

APPROACH: An interdisciplinary approach that combines synthetic inorganic chemistry with template copolymerization techniques is used to immobilize metal complexes in porous organic hosts. New methods have been developed to make porous materials from structurally defined molecular precursors. These include using inert metal complexes as templates to ensure structural homogeneity of immobilized sites. The immobilized metal complexes can be chemically modified to undergo chemical reactions that are not normally observed in solution and can be used for a variety of applications involving molecular recognition.

ACCOMPLISHMENTS: We have designed and synthesized a series of cobalt(2+) complexes immobilized in porous organic hosts that reversibly bind dioxygen under a variety of conditions (e.g., solid-gas, solid-solution). The template techniques developed for these materials created immobilized sites, which have the correct architecture to facilitate efficient dioxygen binding. The architecture of the immobilized sites can be accurately probed by changes in spectroscopic properties of the cobalt(2+) complexes—this study is one of the first to probe these structural properties in template copolymers. In one polymeric system developed in this study, ninety percent of the immobilized cobalt sites reversibly bind dioxygen (160  $\mu\text{mol}$  of  $O_2$ /g of polymer)—this high dioxygen binding capacity is the highest percentage reported for cobalt immobilized in a porous host.

A material was also developed that selectively binds NO, an important environmental and biological molecule. The binding of NO to the immobilized complex induces a color change in the material that can be used in sensor technology. This material is selective for NO over

other biologically relevant gases, such as CO, O<sub>2</sub>, and CO<sub>2</sub>. Moreover, this NO containing material releases NO under biologically relevant conditions (rabbit artery assay). At the submicrogram level of material, > 80% change in the tension of a rabbit artery is observed. This NO-releasing material also inhibits platelet formation. In addition, a small modification of this material produces a NO scavenging materials that can remove NO from a rabbit artery milieu, which causes a constriction in the artery.

A luminescent polymers, containing Eu(III) complexes immobilized in porous organic hosts, have also been developed. The luminescent signals of the polymers are quenched when exposed to benzene. Calibration studies indicate that the porous organic hosts have significant effects on benzene binding. The binding and signal process is completely reversibly.

CONCLUSIONS: These studies showed that template copolymerization is an effective method for designing metal sites in porous organic hosts. The use of substitution inert metal complexes allows for the synthesis of immobilized sites, which are structural similar. The spatial arrangement of ligand groups is relatively fixed within each site; however flexibility in ligand arranges is observed. This flexibility is proposed to occur from the connection between ligand and polymer backbone. Materials made from this method are applicable to gas binding, storage, and released. A large dioxygen binding capacity was observed (160  $\mu$ mol of O<sub>2</sub>/gram of polymer, which means that ~90% of the immobilized metal sites are active. Modification of the immobilized site architecture affords materials that reversible bind nitric oxide. The binding is selective over other biologically relevant gases (e.g., CO, CO<sub>2</sub>, and O<sub>2</sub>) and release is observed under physiological relevant conditions to relax a smooth muscle.

SIGNIFICANCE: These results show that our method for immobilized metal complexes in porous hosts produces functional materials for the reversibly binding analytes. The dioxygen binding capacity for one material developed in this studied is over three times larger than that found for other composite materials, such as cobalt modified zeolites. Storage and release of nitric oxide, a important medicinal compound, shows the potential for developing materials for the delivery of therapeutic agents. Fundamental spectroscopic studies on the immobilized site architecture show that structure can be maintained as designed and templated. These studies were directly probing the inherent structure of the immobilized metal complexes. Importantly, the immobilized sites share properties with their molecular analogues, which bodes well for the further development of materials for a range of applications including, catalysis, sensor technology, and controlling dioxygen concentrations in fuel cells.

PATENT INFORMATION: Patent Pending: METAL COMPLEX/ORGANIC HOST COMPOSITES AND METHODS OF PREPARATION THEREOF; S/N 09/229,247; Filed January 12, 1999; Dkt. 26790.

AWARD INFORMATION: promoted to associate professor with tenure (1998), Vielberth Lecturer, University of Regensburg, Regensburg, Germany (2000).

PUBLICATIONS AND ABSTRACTS

1. Krebs, J. F.; Borovik, A. S. (1998) "Designing Metal Complexes in Porous Organic Hosts," in "Molecular and Ionic Recognition with Imprinted Polymers," ACS Symposium Series 703, R. A. Bartsch and M. Maeda, Eds. American Chemical Society, Washington, DC, 159-170..
2. Krebs, J. F.; Borovik, A. S. (1998) "Dioxygen Binding to Immobilized Co(II) Complexes in Porous Organic Hosts: Evidence for Site Isolation," *Chem. Commun.*, 553-554.
3. Sharma, A.; Borovik, A. S. (2000) "Design, Synthesis and Characterization of Templated Metal Sites in Porous Organic Hosts: Application to Reversible Dioxygen Binding," *J. Am. Chem. Soc.* 122, 8946-8955.
4. Padden, K. M.; Krebs, J. F.; MacBeth, C. E.; Scarrow, R. C.; Borovik, A. S. (2000) "Immobilized Metal Complexes in Porous Organic Hosts: Development of a Material for the Selective and Reversible Binding of Nitric Oxide," submitted.
5. Sharma, A.; Joshi, V.; Borovik, A. S. (2000) "Surface Grafting of Cobalt Complexes on Polymeric Supports: Evidence for Site Isolation and Applications to Reversible Dioxygen Binding," submitted
6. Borovik, A. S. (1996) Immobilized Metal Sites in Porous Organic Hosts as Models for Metalloproteins. Immobilization and Molecular Recognition Gordon Conference. Plymouth, NH.
7. Borovik, A. S. (1997) Immobilized Metal Sites in Porous Organic Hosts as Models for Metalloproteins. Metals in Biology Gordon Conference. Ventura, CA.
8. Borovik, A. S.; Krebs, J. F.; Sharma, A. (1997) Design of Immobilized Metal Sites in Porous Organic Hosts as Models for Metalloproteins: Evidence for Site Isolation. Symposium on Recognition with Imprinted Polymers. American Chemical Society National Meeting. San Francisco, CA.
9. Borovik, A. S. (1997) Design of Immobilized Metal Sites in Porous Organic Hosts as Models for Metalloproteins: Evidence for Site Isolation. NSF Inorganometallic Workshop. Santa Fe, NM.
10. Borovik, A. S. (1998) Design and Synthesis of Immobilized Metal Sites in Porous Organic Hosts. Inorganic Chemistry Gordon Conference. Newport, RI.